

# Mean-Field-Theory for Polymers in Mixed Solvents Thermodynamic and Structural Properties

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Theoretical aspects of polymers in mixed solvents are considered using the Edwards Hamiltonian formalism. Thermodynamic and structural properties are investigated and some predictions are made when the mixed solvent approaches criticality. Both the single and the many chain problems are examined. When the pure mixed solvent is near criticality, addition of a small amount of polymers shifts the criticality towards either enhanced compatibility or induced phase separation depending upon the value of the parameter describing the interaction asymmetry of the solvents with respect to the polymer. The polymer-solvent effective interaction parameter increases strongly when the solvent mixture approaches criticality. Accordingly, the apparent excluded volume parameter decreases and may vanish or even become negative. Consequently, the polymer undergoes a phase transition from a swollen state to an unperturbed state or even take a collapsed configuration. The effective potential acting on a test chain in strong solutions is calculated and the concept of Edwards screening discussed. Structural properties of ternary mixtures of polymers in mixed solvents are investigated within the Edwards Hamiltonian model. It is shown that the effective potential on a test chain in strong solutions could be written as an infinite series expansion of terms describing interactions via one chain, two chains etc. This summation can be performed following a similar scheme as in the Ornstein-Zernike series expansion.

## 1. Introduction

Polymers in mixed solvents show different properties than in individual solvents raising interesting questions from a fundamental point of view<sup>1-6</sup>. Specific features of these systems originate from incompatibility of the two solvents and asymmetry of their interactions with the polymer. If the system exhibits a preferential adsorption of one solvent with the polymer, a difference of solvent composition inside and outside the polymer domain is observed<sup>7-11</sup>. Another peculiar behavior of dilute solutions of polymers in binary mixtures of bad solvents is cosolvency<sup>12-15</sup>. This behavior is quite unexpected since two non solvents for the polymer turn out to present together the properties of a good solvent which is unusual from the point of view of excluded volume effects. If no specific interactions exist between particles in the mixture such as hydrogen bonds or long range electrostatic interaction, one would expect that a mixed solvent exhibits a smooth transition from one solvent quality to the other as the solvent composition changes from 0 to 1 and the solvent power should be an averaged value of its individual components. This is not the case in cosolvent systems where sharp changes characteristic of first order transitions take place. These transitions can be monitored through variations of radii of gyration, second virial coefficients, solution viscosities ... with the solvent composition.

In recent years, with the development of new techniques of polymer characterization using molecular labeling, dyes and neutron scattering techniques, ...widespread research of polymers in mixed solvents has been witnessed in an attempt to understand better their fundamental properties. These mixtures were studied by many authors using different methods such as light and neutron scattering. Mixtures of ordinary and deuterated solvents such as light and heavy water, ordinary and deuterated organic solvents (benzene, toluene ...) are used quite often in neutron scattering measurements to achieve maximum contrast taking advantage of the large difference between the coherent scattering lengths of hydrogen and deuterium atoms<sup>16</sup>.

In polyelectrolyte solutions, a low molecular weight salt is added to increase the ionic strength which weakens the

electrostatic forces and lowers their range. Salt introduces two additional low molecular weight components (co-ions and counter-ions) which could present the properties of mixed solvents<sup>17</sup>.

Recently, mixed solvents were used to study the thermodynamics of polymer brushes<sup>18–20</sup>. Auroy and Auvray<sup>18</sup> observed the collapse-stretching transition of grafted polydimethylsiloxane chains by small angle neutron scattering. Changing temperature and composition, they were able to control the height of the brush. The special boundary conditions in the terminal attachments result into polymer conformation and dynamics which are different from those of the bulk systems. The degree of swelling of polymer brushes is largely determined by the solvent quality. Rothers et al.<sup>20</sup> investigated the swelling of polystyrene (PS) brushes in toluene-methanol mixtures. By changing the solvent composition, they were able to see the collapse-stretching transition in the brush.

Problems involving polymers in mixed solvents are not only of fundamental interest but also they raise interesting concrete questions and offer a large spectrum of practical applications. The increase of amount of water into polymer domains in nylon technology can be monitored directly by NMR imaging techniques and give direct profiles of solvent concentration and ingress dynamics<sup>21,22</sup>. Research efforts are engaged by polymer industries and rayon manufacture to develop new clean methods to meet the requirements of environmental regulations<sup>23</sup>. In these efforts applications of mixed solvent systems are often considered. Polymer synthesis in mixed solvents is another application which is found to allow for a good control of the polymerization process<sup>24,25</sup>.

In this paper, we are interested in the properties of polymers in mixed solvents from the fundamental point of view and present a theoretical investigation based upon the Edwards Hamiltonian formalism<sup>26</sup>. In the next section, we review the case of a single chain in mixed solvents. The effective potential acting on the chain is calculated together with the scattering functions. Phase behavior and chain conformation are obtained from the generalized partition function in the Edwards Hamiltonian formalism. In section 3, we consider the case of strong solutions and discuss changes in the phase behavior and the scattering properties due to the polymer concentration of the medium. Section 4 gives concluding remarks.

## 2. The single chain in mixed solvents

### A. The Edwards Hamiltonian formalism

In this section, we consider infinite dilute solutions of polymers in mixed solvents and use the Edwards Hamiltonian formalism to determine the effective potential exerted on a chain under various conditions of temperature and solvent composition. For simplicity, we assume that all the chains have the same degree of polymerization  $N$  and the same length  $l$  to avoid complications due to polydispersity. For this idealized system, the Edwards Hamiltonian is

$$\begin{aligned} \beta\mathcal{H} = & \frac{3}{2l^2} \int_0^N \left( \frac{\partial \mathbf{R}(s)}{\partial s} \right)^2 ds + \frac{1}{2} \int_0^N \int_0^N V_{PP}[(\mathbf{R}(s) - \mathbf{R}(s'))] ds ds' \\ & + \sum_i \int_0^N V_{AP}[\mathbf{R}(s) - \mathbf{r}_i^A] ds + \sum_i \int_0^N V_{BP}[\mathbf{R}(s) - \mathbf{r}_i^B] ds \\ & + \frac{1}{2} \sum_{i,j}^N V_{AA}[\mathbf{r}_i^A - \mathbf{r}_j^A] + \frac{1}{2} \sum_{i,j} V_{BB}[\mathbf{r}_i^B - \mathbf{r}_j^B] + \sum_{i,j} V_{AB}[\mathbf{r}_i^A - \mathbf{r}_j^B] \end{aligned} \quad (1)$$

where  $\beta = 1/k_B T$ ,  $k_B$  is the Boltzmann constant and  $T$  the absolute temperature,  $\mathbf{R}(s)$  is the chain variable and  $s$  the curvilinear coordinates along the chain (contour variable). The first term in the right hand side (RHS) of equation (1) is the Wiener measure for random walks (assuming that unperturbed chains are Gaussian) and represents the chain entropy due to its elasticity. The other terms in the RHS of equation 1 result from two-body interactions between various particles in the medium either of the same or different species. In this expression, we have used the assumption that the interaction potentials are short ranged and can be approximated with Dirac delta functions

$$V_{ij}(\mathbf{r}_i - \mathbf{r}_j) = V_{ij} \delta(\mathbf{r}_i - \mathbf{r}_j) \quad (2)$$

where  $V_{ij}$  is the strength of the interaction potential between particles  $i$  and  $j$ . Using the standard procedures of functional theory and Edwards Hamiltonian formalism, we derive the thermodynamic and the structural properties of

the mixture under consideration from the generalized partition function. Starting from the Hamiltonian of *equation* 1, one obtains the partition function as a functional integral over all monomers and solvent coordinates

$$\mathcal{Z} = \int \mathcal{D}\mathbf{R}(s) \int \prod_i d\mathbf{r}_i^A \prod_i d\mathbf{r}_i^B \exp[-\beta\mathcal{H}[(\mathbf{R}(s), \mathbf{r}_i^A, \mathbf{r}_i^B)] \quad (3)$$

Where the superscripts  $A$  and  $B$  refer to the solvents. It is quite difficult to handle the partition function in the particle position variable. Rather, it is more convenient to transform into collective variables such as particle densities

$$\begin{aligned} \rho_{\mathbf{q}}^A &= \sum_i \exp(-i\mathbf{q}\mathbf{r}_i^A) \\ \rho_{\mathbf{q}}^B &= \sum_i \exp(-i\mathbf{q}\mathbf{r}_i^B) \end{aligned} \quad (4)$$

Considering the single chain in solution and integrating over solvent coordinates, one obtains the Edwards Hamiltonian for the chain subject to the effective potential  $V_0(\mathbf{q})$

$$\beta\mathcal{H} = \frac{3}{2l^2} \int_0^N \left( \frac{\partial \mathbf{R}(s)}{\partial s} \right)^2 ds + \sum_{\mathbf{q}} \int_0^N ds \int_0^N ds' V_0(\mathbf{q}) \exp[-i\mathbf{q}(\mathbf{R}(s) - \mathbf{R}(s'))] \quad (5)$$

The explicit form of  $V_0(\mathbf{q})$  is obtained following the procedure described below.

### B. The effective potential of a single chain $V_0(\mathbf{q})$

The partition function in equation (3) can be written differently by making use of the collective coordinates  $\rho_{\mathbf{q}}^A$  and  $\rho_{\mathbf{q}}^B$

$$\begin{aligned} \mathcal{Z} = \int \mathcal{D}\mathbf{R}(s) \int \prod_{\mathbf{q}} \delta\rho_{\mathbf{q}}^A \prod_{\mathbf{q}} \delta\rho_{\mathbf{q}}^B \exp[-\frac{3}{2l^2} \int_0^N \left( \frac{\partial \mathbf{R}(s)}{\partial s} \right)^2 ds - \frac{1}{2} V_{PP} \int_0^N \int_0^N ds ds' \delta[\mathbf{R}(s) - \mathbf{R}(s')] \\ - V_{AP} \sum_{\mathbf{q}} \int_0^N \exp(-i\mathbf{q}\mathbf{R}(s)) \rho_{\mathbf{q}}^A - V_{BP} \sum_{\mathbf{q}} \int_0^N \exp(-i\mathbf{q}\mathbf{R}(s)) \rho_{\mathbf{q}}^B \\ - \frac{1}{2} V_{AA} \sum_{\mathbf{q}} |\rho_{\mathbf{q}}^A|^2 - \frac{1}{2} V_{BB} \sum_{\mathbf{q}} |\rho_{\mathbf{q}}^B|^2 - V_{AB} \sum_{\mathbf{q}} \rho_{\mathbf{q}}^A \rho_{-\mathbf{q}}^B] \end{aligned} \quad (6)$$

where the letter  $P$  refers to the polymer. The particle conservation can be expressed by using the following equation

$$\int \prod_{\mathbf{q}} \delta\rho_{\mathbf{q}} \delta \left[ \rho_{\mathbf{q}} - \sum_i \exp(-i\mathbf{q}\mathbf{r}_i) \right] = 1 \quad (7)$$

and introducing field variables via the auxiliary Edwards random fields  $\Phi$

$$\delta[\rho_{\mathbf{q}} - \sum_i \exp(-i\mathbf{q}\mathbf{r}_i)] = \int \delta\Phi_{\mathbf{q}} \exp[-i\Phi_{\mathbf{q}}\rho_{-\mathbf{q}}] \exp[-i\Phi_{\mathbf{q}} \sum_i -i\mathbf{q}\mathbf{r}_i] \quad (8)$$

With straightforward mathematical manipulations, one arrives at

$$\begin{aligned} \mathcal{Z} = \int \mathcal{D}\mathbf{R}(s) \int \prod_{\mathbf{q}} \delta\rho_{\mathbf{q}}^A \prod_{\mathbf{q}} \delta\rho_{\mathbf{q}}^B \exp[-\frac{3}{2l^2} \int_0^N \left( \frac{\partial \mathbf{R}(s)}{\partial s} \right)^2 ds - \frac{1}{2} V_{PP} \int_0^N \int_0^N ds ds' \delta[\mathbf{R}(s) - \mathbf{R}(s')] \\ - V_{AP} \sum_{\mathbf{q}} \int_0^N ds \exp(-i\mathbf{q}\mathbf{R}(s)) \rho_{\mathbf{q}}^A - V_{BP} \sum_{\mathbf{q}} \int_0^N ds \exp(-i\mathbf{q}\mathbf{R}(s)) \rho_{\mathbf{q}}^B \\ - \frac{1}{2} \sum_{\mathbf{q}} (V_{AA} + \frac{1}{S_A}) |\rho_{\mathbf{q}}^A|^2 - \frac{1}{2} \sum_{\mathbf{q}} (V_{BB} + \frac{1}{S_B}) |\rho_{\mathbf{q}}^B|^2 - V_{AB} \sum_{\mathbf{q}} \rho_{\mathbf{q}}^A \rho_{-\mathbf{q}}^B] \end{aligned} \quad (9)$$

For an incompressible mixture, the total mean density fluctuation is zero and one has

$$\rho_{\mathbf{q}}^A + \rho_{\mathbf{q}}^B + \int_0^N ds \exp(-i\mathbf{q}\mathbf{R}(s)) = 0 \quad (10)$$

Substituting this result into equation (9) and integrating over solvent collective coordinates, one obtains the partition function in terms of an effective Hamiltonian  $\mathcal{H}$  given by

$$\beta\mathcal{H} = \frac{3}{2l^2} \int_0^N \left( \frac{\partial \mathbf{R}(s)}{\partial s} \right)^2 ds + \int_0^N \int_0^N V_0(\mathbf{q}) \exp[-i\mathbf{q}(\mathbf{R}(s) - \mathbf{R}(s'))] ds ds' \quad (11)$$

where the effective potential  $V_0(\mathbf{q})$  is function of the potentials  $V_{ij}$  and the partial structure factors  $S_A(\mathbf{q})$  and  $S_B(\mathbf{q})$

$$V_0(\mathbf{q}) = V_{PP} + V_{BB} + \frac{1}{S_B(\mathbf{q})} - 2V_{BP} - \frac{\left( V_{BB} - V_{AB} + V_{AP} - V_{BP} + \frac{1}{S_B(\mathbf{q})} \right)^2}{V_{AA} + V_{BB} - 2V_{AB} + \frac{1}{S_A(\mathbf{q})} + \frac{1}{S_B(\mathbf{q})}} \quad (12)$$

The subscripts of potentials run over polymer  $P$  and solvents  $A$  and  $B$ . To make contact with measurable quantities, it is convenient to express  $V_0(\mathbf{q})$  in terms of the Flory-Huggins interaction parameter  $\chi_{ij}$ .<sup>27</sup>

$$\chi_{ij} = V_{ij} - \frac{V_{ii} + V_{jj}}{2} \quad (13)$$

Combining equations (12) and (13) yields

$$V_0(\mathbf{q}) = \frac{S_A^{-1}(\mathbf{q})S_B^{-1}(\mathbf{q}) - 2\chi_{AP}S_B^{-1}(\mathbf{q}) - 2\chi_{BP}S_A^{-1}(\mathbf{q}) + D}{S_A^{-1}(\mathbf{q}) + S_B^{-1}(\mathbf{q}) - 2\chi_{AB}} \quad (14)$$

where  $D$  is a function of the corresponding Flory-Huggins interaction<sup>1</sup> parameters only

$$D = 2\chi_{AB}\chi_{AP} + 2\chi_{AB}\chi_{BP} + 2\chi_{AP}\chi_{BP} - \chi_{AP}^2 - \chi_{BP}^2 - \chi_{AB}^2 \quad (15)$$

Equation (14) could be written in a different form which is appealing from the point of view of the effective potential acting on a polymer chain in mixed solvents

$$V_0(\mathbf{q}) = \frac{1}{S_B(\mathbf{q})} - 2\chi_{BP}' = \frac{1}{S_B(\mathbf{q})} - 2\chi_{BP} - \frac{(S_B^{-1}(\mathbf{q}) - \chi_{AB} - \chi_{BP} + \chi_{AP})^2}{S_A^{-1}(\mathbf{q}) + S_B^{-1}(\mathbf{q}) - 2\chi_{AB}} \quad (16)$$

Similar results were obtained by others and in particular by Schultz and Flory<sup>1</sup> and by Benoit and Strazielle<sup>28</sup> using different methods of the mean field theory. The Edwards Hamiltonian method gives another route for deriving the effective potential on a chain together with the scattering properties. It has the merit of showing the response of a polymer chain undergoing interaction from the mixed solvent under various conditions of temperature, composition, etc.

### C. The scattering functions

In the following subsection the crudest approximation that can be imagined. Although we consider only one chain in the mixed solution we use a mean field description of the RPA form. We are aware that this approximation is very bad indeed, nevertheless it is used here to see the principal influence of the binary solvent on the interaction potentials. Has we used Gaussian chains this approximation would be fine. This case belongs to  $V_{PP} = 0$ . Another possibility of slight improvement is to treat the polymer plus excluded volume interaction as effectively "bare" system and use an appropriate Padé approximation including the selfavoiding walk exponent  $\nu \approx 3/5$ .

Starting from equation 11, after some straightforward manipulations, one could write the Edwards Hamiltonian in terms of the scattering functions for incompressible mixtures of polymers and mixed solvents. The following

conventional notation is adopted. For interaction potentials, we keep the subscript  $P$  for all the polymer chains but for the single chain structure factor we use the subscript 1 meaning a single test chain. With this convention, the Edwards Hamiltonian becomes

$$\begin{aligned}\beta\mathcal{H} = & \sum_{\mathbf{q}} [S_1^{-1}(\mathbf{q}) + V_{PP} + V_{BB} + S_B^{-1}(\mathbf{q}) - 2V_{BP}] |\rho_{\mathbf{q}}^1|^2 \\ & + [V_{AP} - V_{BP} - V_{AB} + V_{BB} + S_B^{-1}(\mathbf{q})] \rho_{\mathbf{q}}^1 \rho_{-\mathbf{q}}^A \\ & + \frac{1}{2} [V_{AA} + S_A^{-1}(\mathbf{q}) + V_{BB} + S_B^{-1}(\mathbf{q}) - 2V_{AB}] |\rho_{\mathbf{q}}^A|^2\end{aligned}\quad (17)$$

The above equation takes a greatly simplified form in the matrix notation

$$\beta\mathcal{H} = \frac{1}{2} \sum_{\mathbf{q}} \vec{\rho}_{\mathbf{q}}^T \vec{S}(\mathbf{q})^{-1} \vec{\rho}_{-\mathbf{q}} \quad (18)$$

where  $\vec{\rho}$  is a column vector

$$\vec{\rho}(\mathbf{q}) = \begin{pmatrix} \rho_{\mathbf{q}}^1 \\ \rho_{\mathbf{q}}^A \end{pmatrix} \quad (19)$$

$\vec{\rho}^T$  is its transpose and  $\vec{S}(\mathbf{q})$  is a second rank square matrix whose elements depend upon the single particle structure factors  $S_A^0(\mathbf{q})$ ,  $S_B^0(\mathbf{q})$ ,  $S_1^0(\mathbf{q})$  and the Flory-Huggins interaction parameters  $\chi_{AB}$ ,  $\chi_{BP}$ , and  $\chi_{AP}$ .

$$\vec{S}^{-1}(\mathbf{q}) = \begin{pmatrix} S_1^{-1}(\mathbf{q}) + S_B^{-1}(\mathbf{q}) - 2\chi_{BP} & S_B^{-1}(\mathbf{q}) - \chi_{AB} - \chi_{BP} + \chi_{AP} \\ S_B^{-1}(\mathbf{q}) - \chi_{AB} - \chi_{BP} + \chi_{AP} & S_A^{-1}(\mathbf{q}) + S_B^{-1}(\mathbf{q}) - 2\chi_{AB} \end{pmatrix} \quad (20)$$

Inversion of this matrix gives the partial structure factors  $S_{11}(\mathbf{q})$ ,  $S_{AA}(\mathbf{q})$  and  $S_{A1}(\mathbf{q})$

$$S_{11}(\mathbf{q}) = \frac{S_A^{-1}(\mathbf{q}) + S_B^{-1}(\mathbf{q}) - 2\chi_{AB}}{(S_1^{-1}(\mathbf{q}) + S_B^{-1}(\mathbf{q}) - 2\chi_{BP})(S_A^{-1}(\mathbf{q}) + S_B^{-1}(\mathbf{q}) - 2\chi_{AB}) - (S_B^{-1}(\mathbf{q}) - \chi_{BP} - \chi_{AB} + \chi_{AP})^2} \quad (21)$$

$$S_{AA}(\mathbf{q}) = \frac{S_1^{-1}(\mathbf{q}) + S_B^{-1}(\mathbf{q}) - 2\chi_{BP}}{(S_1^{-1}(\mathbf{q}) + S_B^{-1}(\mathbf{q}) - 2\chi_{BP})(S_A^{-1}(\mathbf{q}) + S_B^{-1}(\mathbf{q}) - 2\chi_{AB}) - (S_B^{-1}(\mathbf{q}) - \chi_{BP} - \chi_{AB} + \chi_{AP})^2} \quad (22)$$

$$\begin{aligned}S_{A1}(\mathbf{q}) &= S_{1A}(\mathbf{q}) \\ &= - \frac{S_B^{-1}(\mathbf{q}) - \chi_{AB} - \chi_{BP} + \chi_{AP}}{(S_1^{-1}(\mathbf{q}) + S_B^{-1}(\mathbf{q}) - 2\chi_{BP})(S_A^{-1}(\mathbf{q}) + S_B^{-1}(\mathbf{q}) - 2\chi_{AB}) - (S_B^{-1}(\mathbf{q}) - \chi_{BP} - \chi_{AB} + \chi_{AP})^2}\end{aligned} \quad (23)$$

These results can be used to extract the properties of the mixture both in the thermodynamic limit by letting  $q = 0$  and at finite  $q$  where we can explore the chain conformation and the spatial distribution of particles within the medium. We first consider the thermodynamic limit in the following section.

### 1. The thermodynamic limit $\mathbf{q} = 0$

In this limit  $q = 0$  and equations (21) and (22) become

$$S_{11}^{-1} = \phi_1^{-1} + \phi_B^{-1} - 2 \left( \chi_{BP} + \frac{(\phi_B^{-1} - \chi_{AB} - \chi_{BP} + \chi_{AP})^2}{2(\phi_A^{-1} + \phi_B^{-1} - 2\chi_{AB})} \right) \quad (24)$$

$$S_{AA}^{-1} = \phi_A^{-1} + \phi_B^{-1} - 2 \left( \chi_{AB} + \frac{(\phi_B^{-1} - \chi_{AB} - \chi_{BP} + \chi_{AP})^2}{2(\phi_1^{-1} + \phi_B^{-1} - 2\chi_{BP})} \right) \quad (25)$$

For simplicity, we remove the argument  $\mathbf{q}$  from the structure factor in the thermodynamic limit  $\mathbf{q} = 0$ . We consider a mixed solvent in the vicinity of the critical temperature  $T_c$  where  $\chi_{AB}$  is close to the critical value  $\chi_c$  and show how a small amount of polymer added to the mixture shifts the criticality condition. We also examine the way in which the chain responds to the approach towards solvent criticality condition.

In the pure solvent mixture when  $\mathbf{q} = 0$ , one has

$$S_{AA}^{-1} = 2(\chi_c - \chi_{AB}) \quad (26)$$

which can be obtained from equation (25) by letting  $\phi_1 = 0$ ;  $\chi_c$  is the critical parameter for phase separation which is function of the solvent composition only

$$\chi_c = \frac{1}{2}(\phi_A^{-1} + \phi_B^{-1}) \quad (27)$$

If polymer is added to the solution, the partial structure factor in the forward direction  $S_{AA}$  becomes function of the polymer volume fraction  $\phi_1$  and can be written as

$$S_{AA}^{-1} = 2(\chi'_c - \chi_{AB}) \quad (28)$$

This result shows that the critical parameter undergoes a shift by an amount  $\Delta\chi_c$

$$\Delta\chi_c = \chi'_c - \chi_c = -\frac{(\phi_B^{-1} - \chi_{AB} - \chi_{BP} + \chi_{AP})^2}{2(\phi_1^{-1}N_1^{-1} + \phi_B^{-1} - 2\chi_{BP})} \quad (29)$$

One observes that the critical parameter  $\chi'_c = \chi_c + \Delta\chi_c$  either increases or decreases depending upon the sign of  $\Delta\chi_c$  which in turn is fixed by the sign of the denominator in equation (29). This sign is determined by the relative magnitude of  $\chi_{BP}$  as compared to  $\frac{1}{2\phi_1N_1} + \frac{1}{2\phi_B}$ . If  $\chi_{BP}$  the interaction between polymer and solvent B is smaller than  $\frac{1}{2\phi_1N_1} + \frac{1}{2\phi_B}$ , the quantity  $\Delta\chi_c$  is negative and the critical parameter decreases (i.e.  $\chi'_c < \chi_c$ ). This means that the polymer favors solvent demixing since a smaller interaction drives the solvents to the limit of stability. For example, choosing  $N_1 = 100$ ,  $\phi_1 = 0.01$  and  $\phi_B = 0.495$ , gives  $\frac{1}{2\phi_1N_1} + \frac{1}{2\phi_B} = 1.5$ . This means that if  $\chi_{BP}$  is smaller than 1.5,  $\Delta\chi_c$  is negative and addition of a small amount of polymer (approximately 1 percent) induces phase separation of the solvent mixture. If  $\chi_{BP}$  is higher than 1.5, the system behaves differently since addition of polymer would result into a positive  $\Delta\chi_c$  indicating compatibility enhancement of the solvent mixture. The mixture phase separates only under a strong repulsion between A and B solvents. These features can be observed in *figure 1* where  $\chi'_c$  is plotted against  $\phi_1$  for two values of  $\chi_{BP}$ . One observes different tendencies, depending upon the value of the interaction parameter  $\chi_{BP}$ . For the lower value, there is a slight decrease of  $\chi'_c$  upon addition of polymer. If  $\chi_{BP}$  is as high as 1.5 expressing a large polymer-solvent B incompatibility, a small amount of polymer would result into a large increase of  $\Delta\chi_c$  meaning that the solvents A and B prefer to remain mixed rather than adsorbing on the polymer even though the interaction  $\chi_{AB}$  chosen in plotting this figure ( $\chi_{AB} = 1$ ) is relatively high. This compatibility enhancement of the mixed solvent due to the presence of polymer is quite spectacular since  $\chi'_c$  increases by practically an order of magnitude upon addition of a small amount of polymer. Qualitatively, this behavior is consistent with the observation made on PS/(benzene+cyclohexane) by Varra and Autalik<sup>29</sup>. These authors found that a strong interactions between PS and non solvents (cyclohexane) could lead to a reduced solvent-solvent interaction and hence a compatibility enhancement of the mixture. Furthermore, one finds that the shift  $\chi'_c - \chi_c = \Delta\chi_c$  is only moderately sensitive to the interaction asymmetry between the polymer and the solvents A and B which is expressed by the parameter  $\epsilon = \chi_{BP} - \chi_{AP}$ . The shift in the critical parameter  $\Delta\chi_c$  is strong upon addition of polymer even for small values of  $\epsilon$ . The interaction asymmetry parameter plays a more crucial role in connection with the polymer conformation near the solvent criticality condition as we shall see in the following section.

The effective potential  $V_0$  of equation (16) is directly related to the classical excluded volume parameter acting on a polymer in the infinite dilute limit. This is made clear by writing the partial structure factor  $S_{11}(\mathbf{q})$  in the reciprocal form similar to Zimm's equation

$$S_{11}^{-1}(\mathbf{q}) = S_1^{-1}(\mathbf{q}) + V_0 \quad (30)$$

Letting  $\Delta\chi_0 = \chi_c - \chi_{AB}$  one obtains

$$V_0 = \frac{1}{\phi_B} - 2\chi_{BP} - \frac{(\Delta\chi_0 + \epsilon)^2}{2\Delta\chi_0} \quad (31)$$

For an upper critical solution temperature mixture, the interaction parameter  $\chi_{AB}$  increases approaching  $\chi_c$ . In this case, the polymer reacts in different ways depending essentially on whether  $\epsilon$  is zero or not. This is a clear illustration of the importance of interaction asymmetry between polymer and solvents in determining the thermodynamic behavior of the solution. As the solvent mixture approaches the criticality condition ( $\Delta\chi_0 \rightarrow 0$ ), a striking difference exists between the case where the solvents present the same interaction with the polymer ( $\epsilon = 0$ ) and the case where the two solvents interact differently with the polymer ( $\epsilon \neq 0$ ). Equation (31) shows that in the case of a symmetric interaction ( $\epsilon = 0$ ),  $V_0$  decreases linearly with  $\Delta\chi_0$ . However, in the non symmetric interaction problem ( $\epsilon \neq 0$ ), the third term in the RHS of equation (31) increases rapidly as  $\Delta\chi_0 \rightarrow 0$  and  $V_0$  undergoes a rapid decrease. Following this sharp decrease, the effective potential vanishes and may even become negative as  $\chi_{AB}$  approaches  $\chi_c$ . The chain undergoes a phase transition from a swollen state to unperturbed dimensions or even a collapsed configuration. This is illustrated in *figure 2* where  $V_0$  is represented as a function of  $\Delta\chi_0$  for  $\epsilon = 0$  and 0.2. The upper curve in this figure corresponds to the case where the interaction between polymer and solvents A and B are the same and  $\epsilon = 0$ . It shows that  $V_0$  increases relatively smoothly when  $\Delta\chi_0 \rightarrow 0$ .

One could also introduce an effective polymer-solvent interaction parameter  $\chi_0$  via

$$V_0 = \frac{1}{\phi_B} - 2\chi_0 \quad (32)$$

With

$$\chi_0 = \chi_{BP} + \frac{(\Delta\chi_0 + \epsilon)^2}{4\Delta\chi_0} \quad (33)$$

*Figure 3* represents the variation of the effective polymer-solvent interaction parameter  $\chi_0$  as a function of  $\Delta\chi_0$  for the same values of  $\epsilon$  as in *figure 2* and shows similar tendencies. For  $\epsilon = 0$ ,  $\chi_0$  decreases slightly when  $\Delta\chi_0 \rightarrow 0$ , while for  $\epsilon = 0.2$ , there is an inversion in the variation of  $\chi_0$  expressed by a turn up and a sharp increase as the mixed solvent approaches criticality indicating a strong polymer-solvent repulsion.

## 2. The small $\mathbf{q}$ limit

As a first approximation, we consider that  $q^{-1} \gg 1$  which means that by scattering radiation, one observes the solvent particles as point like and the  $q$ -dependence comes entirely from the form factor of the polymer only. This approximation could be easily relaxed if one wants to include intramolecular interferences within the solvent particles themselves and explore by radiation scattering the internal structure of chains. Moreover, we will assume that the form factor of the chain could be approximated by

$$P(q) = \frac{1}{1 + \frac{q^2 R_g^2}{2}} \quad (34)$$

Following these assumptions, equation (17) can be written in the form

$$S_{11}(q) = \frac{S_{11}(q=0)}{1 + q^2 \xi_0^2} \quad (35)$$

Where the correlation length  $\xi_0$  represents the distance over which the polymer configuration is sensitive to solvent fluctuations. It depends upon the polymer radius of gyration  $R_g$  and the excluded volume interaction  $V_0$  according to the relationship

$$\xi_0^2 = \frac{R_g^2}{2(1 + V_0 \phi_1 N_1)} \quad (36)$$

*Figure(4)* represents the variation of  $\xi_0/R_g$  as a function of  $\Delta\chi_0$  for  $\epsilon = 0$  and 0.2. For  $\epsilon = 0$ ,  $\xi_0/R_g$  decreases continuously when  $\Delta\chi_0 \rightarrow 0$  while for  $\epsilon = 0.2$ ,  $\xi_0/R_g$  increases suddenly when  $\Delta\chi_0$  approaches zero. One can

visualize the polymer as a chain of blobs of size  $\xi_0$ . Over distances below the blob size, the chain is sensitive to solvent fluctuations and its size reduces as a result of increasing effective interaction  $\chi_0$ . Over distances exceeding the blob size, the chain does not feel the effects of solvent fluctuations and shows a comparatively swollen conformation. As the solvent approaches criticality when  $\Delta\chi_0 \rightarrow 0$ , the correlation length  $\xi_0$  becomes comparable or larger than  $R_g$  implying that the entire chain is subject to solvent fluctuations and undergoes a phase transition from a swollen to a more compact conformation. For  $\epsilon = 0$  and  $\chi_{BP} = \chi_{AP} = 0.5$ , the chain feels theta solvent conditions even though  $\Delta\chi_0 \rightarrow 0$  and solvents demixing conditions are approached.

The blob picture for a polymer in mixed solvents was first suggested by Brochard and de Gennes<sup>3</sup> who examined the polymer conformation in a mixture of two good solvents, when the polymer affinity differs substantially for the two solvents. They were the first to predict that the polymer adopts a collapsed configuration near  $T_c$  even it would be swollen in either of the pure solvents under similar conditions.

### 3. Many chains in mixed solvents

#### A. The effective potential of a test chain

In this section, we discuss the problem of many chains by extending the Edwards Hamiltonian formalism to strong solutions of polymers and mixed solvents. The effective potential acting on a test chain together with partial structure factors are calculated as a function of polymer concentration and mixed solvent properties. The Hamiltonian formalism is extended by taking into account the effects of the many chains present in the medium. This gives the following result for the partition function including summations over all chains designated by the letters  $\alpha$  and  $\beta$

$$\begin{aligned} \mathcal{Z} = & \int \prod \mathcal{D}\mathbf{R}_\alpha(s) \int \prod d\vec{\mathbf{r}}_i^A \prod d\vec{\mathbf{r}}_i^B \exp \left[ -\frac{3}{2l^2} \sum_\alpha \int_0^N \left( \frac{\partial \mathbf{R}_\alpha(s)}{\partial s} \right)^2 ds \right. \\ & - \frac{1}{2} V_{PP} \sum_{\alpha\beta} \int_0^N \int_0^N \delta(\mathbf{R}_\alpha(s) - \mathbf{R}_\beta(s')) ds ds' \\ & - V_{AP} \sum_\alpha \int_0^N \sum_i \delta(\mathbf{R}_\alpha(s) - \mathbf{r}_i^A) ds - V_{BP} \sum_\alpha \int_0^N \sum_i \delta(\mathbf{R}_\alpha(s) - \mathbf{r}_i^B) ds \\ & \left. - \frac{1}{2} V_{AA} \sum_{ij} (\mathbf{r}_i^A - \mathbf{r}_j^A) - \frac{1}{2} V_{BB} \sum_{ij} (\mathbf{r}_i^B - \mathbf{r}_j^B) - V_{AB} \sum_{ij} \delta(\mathbf{r}_i^A - \mathbf{r}_j^B) \right] \end{aligned} \quad (37)$$

The subscript  $\alpha$  and  $\beta$  run over all chains in the solution except a test chain designated by the subscript 1 (meaning single). Transforming space coordinates into collective density variables leads to the partition function

$$\begin{aligned} \mathcal{Z} = & \int \mathcal{D}\mathbf{R}_1(s) \int \prod \delta\rho_{\mathbf{q}}^A \prod \delta\rho_{\mathbf{q}}^B \exp \left[ -\frac{3}{2l^2} \int_0^N \left( \frac{\partial \mathbf{R}_1(s)}{\partial s} \right)^2 ds - \frac{1}{2} V_{PP} |\rho^1|^2 \right. \\ & - V_{PP} \sum_{\mathbf{q}} |\rho_{\mathbf{q}}^P| |\rho_{\mathbf{q}}^1| - \frac{1}{2} \sum_{\mathbf{q}} (V_{PP} + S_P^{-1}(\mathbf{q})) |\rho_{\mathbf{q}}^P|^2 \\ & - V_{AP} \sum_{\mathbf{q}} \rho_{\mathbf{q}}^1 \rho_{-\mathbf{q}}^A - V_{AP} \sum_{\mathbf{q}} \rho_{\mathbf{q}}^P \rho_{-\mathbf{q}}^A - V_{BP} \sum_{\mathbf{q}} \rho_{\mathbf{q}}^1 \rho_{-\mathbf{q}}^B - V_{BP} \sum_{\mathbf{q}} |\rho_{\mathbf{q}}^P| |\rho_{\mathbf{q}}^B| \\ & \left. - \frac{1}{2} \sum_{\mathbf{q}} (V_{AA} + S_A^{-1}(\mathbf{q})) |\rho_{\mathbf{q}}^A|^2 - \frac{1}{2} \sum_{\mathbf{q}} (V_{BB} + S_B^{-1}(\mathbf{q})) |\rho_{\mathbf{q}}^B|^2 - \sum_{\mathbf{q}} V_{AB} \rho_{\mathbf{q}}^A \rho_{-\mathbf{q}}^B \right] \end{aligned} \quad (38)$$

Where  $\rho_{\mathbf{q}}^A$  and  $\rho_{\mathbf{q}}^B$ ,  $\rho_{\mathbf{q}}^P$  and  $\rho_{\mathbf{q}}^1$  are the collectives coordinates for the solvents  $A$  and  $B$ , the polymer  $P$  and the test chain 1, respectively. In order to identify the effective potential acting on a test chain together with the partial scattering functions for the multicomponent mixture under investigation, it is convenient to write the partition function in matrix form



$$\mathcal{Z} = \int \mathcal{D}\mathbf{R}_1(s) \int \prod \delta\vec{\rho}_{\mathbf{q}} \exp \left[ -\frac{3}{2l^2} \int_0^N \left( \frac{\partial \mathbf{R}_1(s)}{\partial s} \right)^2 ds - \frac{1}{2} V_{\text{PP}} \sum |\rho_{\mathbf{q}}^1|^2 \right] \exp \left[ -\sum 2\vec{\mathbf{V}}(\mathbf{q})\vec{\rho}_{\mathbf{q}} - \sum \vec{\rho}_{\mathbf{q}}^{-1} \vec{\mathbf{M}}(\mathbf{q})\vec{\rho}_{-\mathbf{q}} \right] \quad (39)$$

where  $\vec{\rho}_{\mathbf{q}}$  and  $\vec{\mathbf{V}}(\mathbf{q})$  represent the column vectors

$$\vec{\rho}_{\mathbf{q}} = \begin{pmatrix} \rho_{\mathbf{q}}^{\text{A}} \\ \rho_{\mathbf{q}}^{\text{B}} \\ \rho_{\mathbf{q}}^{\text{P}} \end{pmatrix} \quad (40)$$

$$\vec{\mathbf{V}}(\mathbf{q}) = \begin{pmatrix} \frac{1}{2} V_{\text{AP}} \int_0^N \exp(-i\mathbf{q}\mathbf{R}(s)ds) \\ \frac{1}{2} V_{\text{BP}} \int_0^N \exp(-i\mathbf{q}\mathbf{R}(s)ds) \\ \frac{1}{2} V_{\text{PP}} \int_0^N \exp(-i\mathbf{q}\mathbf{R}(s)ds) \end{pmatrix} \quad (41)$$

and  $\vec{\mathbf{M}}(\mathbf{q})$  is a square three-by-three matrix

$$\vec{\mathbf{M}}(\mathbf{q}) = \begin{pmatrix} \frac{1}{2}(V_{\text{AA}} + \frac{1}{S_{\text{A}}(\mathbf{q})}) & \frac{1}{2}V_{\text{AB}} & \frac{1}{2}V_{\text{AP}} \\ \frac{1}{2}V_{\text{AB}} & \frac{1}{2}(V_{\text{BB}} + \frac{1}{S_{\text{B}}(\mathbf{q})}) & \frac{1}{2}V_{\text{BP}} \\ \frac{1}{2}V_{\text{AP}} & \frac{1}{2}V_{\text{BP}} & \frac{1}{2}(V_{\text{PP}} + \frac{1}{S_{\text{P}}(\mathbf{q})}) \end{pmatrix} \quad (42)$$

Integrating over the collective variables  $\rho_{\mathbf{q}}$ , one obtains the partition function as follows

$$\mathcal{Z} = \int \mathcal{D}\mathbf{R}_1(s) \exp \left[ -\frac{3}{2l^2} \int_0^N \left( \frac{\partial \mathbf{R}(s)}{\partial s} \right)^2 ds - \frac{1}{2} V_{\text{PP}} \sum_{\mathbf{q}} |\rho_{\mathbf{q}}^1|^2 + \sum_{\mathbf{q}} \vec{\mathbf{V}}_{\mathbf{q}}^{-1} \vec{\mathbf{M}}_{\mathbf{q}}^{-1} \vec{\mathbf{V}}_{\mathbf{q}} \right] \quad (43)$$

Recalling that  $\mathcal{Z} = \int \mathcal{D}\mathbf{R}_1(s) \exp -\beta\mathcal{H}$  yields

$$\beta\mathcal{H} = \frac{3}{2l^2} \int_0^N \left( \frac{\partial \mathbf{R}(s)}{\partial s} \right)^2 ds + \sum_{\mathbf{q}} V(\mathbf{q}) \int_0^N \int_0^N ds ds' \exp(-i\mathbf{q}(\mathbf{R}(s) - \mathbf{R}(s'))) \quad (44)$$

where one can identify the effective potential  $V_{\mathbf{q}}$  acting on a test chain. If the volumes occupied by monomers and solvent molecules are the same, then  $V_{\text{PP}}$ ,  $V_{\text{AA}}$  and  $V_{\text{BB}}$  are approximately represented by the same quantity denoted  $V_{\infty}$  and one can introduce the Flory-Huggins interaction parameters using  $V_{\infty} = V_{ij} - \chi_{ij}$  where the subscripts i and j run over A, B and P. All polymer chains in the medium have the same interaction parameters and no distinction exists between the test chain 1 and the others. The effective potential  $V(\mathbf{q})$  is not only due to the solvents but also to all the chains present in the medium. For incompressible mixtures, the potential  $V_{\infty}$  goes to infinity and one obtains

$$V(\mathbf{q}) = \frac{S_{\text{A}}^{-1}(\mathbf{q})S_{\text{B}}^{-1}(\mathbf{q}) + D - 2\chi_{\text{AP}}S_{\text{B}}^{-1}(\mathbf{q}) - 2\chi_{\text{BP}}S_{\text{A}}^{-1}(\mathbf{q})}{S_{\text{A}}^{-1}(\mathbf{q}) + S_{\text{B}}^{-1}(\mathbf{q}) - 2\chi_{\text{AB}} + S_{\text{P}}(\mathbf{q})(S_{\text{A}}^{-1}(\mathbf{q})S_{\text{B}}^{-1}(\mathbf{q}) + D - 2\chi_{\text{AP}}S_{\text{B}}^{-1}(\mathbf{q}) - 2\chi_{\text{BP}}S_{\text{A}}^{-1}(\mathbf{q}))} \quad (45)$$

Here D is defined in equation (15). It is interesting to note that the effective potentials acting on chains in infinitely dilute solutions  $V_0(\mathbf{q})$  and in strong solutions  $V(\mathbf{q})$  are related via

$$V^{-1}(\mathbf{q}) = V_0^{-1}(\mathbf{q}) + S_{\text{P}}(\mathbf{q}) \quad (46)$$

This result is characteristic of the series expansion in the Ornstein-Zernike model<sup>30</sup>. It suggests that one can write the total potential  $V(\mathbf{q})$  as an infinite series of interaction terms. The order of these terms depends on the number of intermediate chains involved in the interaction (see *figure 5a*). Each diagram corresponds to a particular term in the series expansion

$$V(\mathbf{q}) = V_0(\mathbf{q}) - V_0(\mathbf{q})S_{\text{P}}(\mathbf{q})V_0(\mathbf{q}) + V_0(\mathbf{q})S_{\text{P}}(\mathbf{q})V_0(\mathbf{q})S_{\text{P}}(\mathbf{q})V_0(\mathbf{q}) + \dots \quad (47)$$

These series can be summed up in a similar way as in the Ornstein-Zernike expansion ( see figure 5b). The summation gives

$$V(\mathbf{q}) = V_0(\mathbf{q}) - V_0(\mathbf{q})S_P(\mathbf{q})V(\mathbf{q}) \quad (48)$$

which is equivalent to

$$V(\mathbf{q}) = V_0(\mathbf{q}) [1 + V_0(\mathbf{q})S_P(\mathbf{q})]^{-1} \quad (49)$$

## B. The Edwards screening

For completeness, we remark that the Edwards screening can be recovered. The effective potential for many chains in equation (47) can also be written in the following form

$$V(\mathbf{q}) = V_0(\mathbf{q}) - \frac{V_0^2(\mathbf{q})}{S_P^{-1}(\mathbf{q}) + V_0(\mathbf{q})} \quad (50)$$

Using Edwards prescription for the form factor of Gaussian chains

$$S_P = \frac{\phi_P N_P}{1 + \frac{1}{2} q^2 R_g^2} \quad (51)$$

where the radius of gyration is related to the degree of polymerization  $N$  and segment length  $l$  by the known result  $R_g = l\sqrt{N/6}$ . Substituting equation 51 into 50 yields

$$\frac{V}{V_0} = \frac{q^2 \xi^2}{1 + q^2 \xi^2} \quad (52)$$

Where  $\xi$  is the Edwards screening length

$$\xi = \frac{l}{\sqrt{12V_0\phi_P}} \quad (53)$$

In the infinite dilute limit,  $\phi_P$  goes to zero and the screening length  $\xi$  tends to infinity. As one would expect, the effective potential  $V$  tends to  $V_0$  in this limit. Figure 6 represents the ratio  $V/V_0$  versus  $q\xi$  as given by equation 52. The ratio  $V/V_0$  is small for  $q\xi$  less than 1 indicating screening of the potential field acting on a test chain. When  $q\xi$  increases the ratio  $V/V_0$  tends to 1 and the effective potential is practically the same as in infinite dilute solutions. Locally at large  $q$ , the test chain behaves as if it were isolated and is essentially not perturbed by the presence of other chains in the medium. It feels only the fluctuations of the solvent mixture in its immediate vicinity.

This analysis of screening presented here and following the Edwards prescription is only qualitative. A more precise treatment is needed if one wants to have a quantitative evaluation of the screening effects. Such an improvement can be made using other methods such as renormalization group theory methods or field theoretical tools<sup>31,32,6</sup>.

## C. The scattering functions

The scattering matrix can be readily extracted from the partition function in the matrix notation

$$\mathbf{S}^{-1}(\mathbf{q}) = \begin{pmatrix} S_I^{-1}(\mathbf{q}) + S_B^{-1}(\mathbf{q}) - 2\chi_{BP} & S_B^{-1}(\mathbf{q}) - 2\chi_{BP} & S_B^{-1}(\mathbf{q}) - \chi_{AB} - \chi_{BP} + \chi_{AP} \\ S_B^{-1}(\mathbf{q}) - 2\chi_{BP} & S_P^{-1}(\mathbf{q}) + S_B^{-1}(\mathbf{q}) - 2\chi_{BP} & S_B^{-1}(\mathbf{q}) - \chi_{AB} - \chi_{BP} + \chi_{AP} \\ S_B^{-1}(\mathbf{q}) - \chi_{AB} - \chi_{BP} + \chi_{AP} & S_B^{-1}(\mathbf{q}) - \chi_{AB} - \chi_{BP} + \chi_{AP} & S_A^{-1}(\mathbf{q}) + S_B^{-1}(\mathbf{q}) - 2\chi_{AB} \end{pmatrix} \quad (54)$$

The diagonal elements of the scattering matrix  $S(\mathbf{q})$  define the contribution to the scattering signal due to different constituents in the mixture. Three quantities are particularly relevant for our purpose in the present work. Considering the solvent  $B$  as a background medium, one can obtain the diagonal elements of equation (54) denoted  $S_{11}(\mathbf{q})$ ,  $S_{PP}(\mathbf{q})$  and  $S_{AA}(\mathbf{q})$ . The properties of these partial structure factors are briefly discussed below.

### 1. Structure factor of a test chain $S_{11}(\mathbf{q})$

The first element of the matrix in equation (54) gives the scattering function from the test chain

$$S_{11}^{-1}(\mathbf{q}) = S_1^{-1}(\mathbf{q}) + V_1(\mathbf{q}) \quad (55)$$

where  $V_1(\mathbf{q})$  is identical to  $V(\mathbf{q})$  given in equation (46). The subscript 1 is introduced to describe a generalized excluded volume experienced by a test chain labeled 1 in the strong solution. Discussion of the screening presented above could be applied here invoking the excluded volume interaction experienced by the test chain 1. It is worthwhile to note that if the mixed solvent satisfies the criticality condition in the absence of polymer, then  $\frac{1}{S_A} + \frac{1}{S_B} = 2\chi_{AB}$ , and equations (55) and (45) give

$$\frac{1}{S_{11}} = \frac{1}{S_P} + \frac{1}{S_1} \quad (56)$$

This result corresponds to the scattering function, one obtains from a solution of identical chains under theta conditions where excluded volume interactions are completely screened out. It is consistent with the variation of  $V_0$  versus  $\Delta\chi_0$  which shows that the apparent excluded volume tends to 0 as  $\Delta\chi_0 \rightarrow 0$  (figure 2)

### 2. Structure factor of the polymer $S_{PP}(\mathbf{q})$

The second diagonal term of the scattering matrix  $S(\mathbf{q})$  represents the contribution from the polymer and found as

$$S_{PP}^{-1}(\mathbf{q}) = S_P^{-1}(\mathbf{q}) + V_P(\mathbf{q}) \quad (57)$$

Where  $V_P(\mathbf{q})$  has a similar expression as  $V_1(\mathbf{q})$  except that  $S_P(\mathbf{q})$  and  $S_1(\mathbf{q})$  are interchanged. If the mixed solvent approaches criticality, the signal from the p-chains become identical to the signal from the test chain 1 and hence the same as in equation (56). The chains are under theta condition as indicated earlier.

### 3. Structure factor of the mixed solvent $S_{AA}(q)$

The third diagonal element of the matrix in equation (54) gives the partial structure factor of the mixed solvent

$$S_{AA}^{-1}(\mathbf{q}) = S_A^{-1}(\mathbf{q}) + S_B^{-1}(\mathbf{q}) - 2\chi_{AB} - \frac{2(S_B^{-1}(\mathbf{q}) - \chi_{AB} - \chi_{BP} + \chi_{AP})^2(S_1^{-1}(\mathbf{q}) + S_P^{-1}(\mathbf{q}))}{(S_P^{-1}(\mathbf{q}) + S_1^{-1}(\mathbf{q}))(S_B^{-1}(\mathbf{q}) - 2\chi_{BP}) + S_1^{-1}(\mathbf{q})S_P^{-1}(\mathbf{q})} \quad (58)$$

In the infinite dilute limit  $S_P = 0$  and one recovers the former result given in equation (22). Considering the  $q = 0$  limit, one can make similar remarks as those following equation (29), except that the concentration range of polymer is not limited to infinite dilute solutions and the polymer concentration range is extended to higher values in investigating the variation of the interaction parameter  $\chi'_c$  as a function of polymer concentration  $\phi_P$ .

## 4. Conclusions

In this paper, we present some theoretical aspects of polymers in mixed solvents using the Edwards Hamiltonian formalism. Discussions are confined to thermodynamic and structural properties and both the single and the many chain problems are considered. If one solvent species presents a strong repulsion towards the polymer, addition of a small amount of polymer leads to compatibility enhancement of the solvent mixture. The critical parameter at which the solvent mixture phase separates increases dramatically. The effective potential acting on the polymer in the medium depends enormously on the asymmetry in the affinity of the polymer with respect to both solvent species. If this asymmetry is large, as the mixed solvent approaches the criticality condition, the effective interaction polymer-solvent increases dramatically. The polymer undergoes a phase transition from a swollen configuration

to unperturbed dimensions and eventually to a collapsed configuration as the mixed solvent approaches criticality. When the correlation length for solvent fluctuations is of the order or higher than the radius of gyration of polymer  $R_g$ , the chain conformation becomes characteristic of a polymer in bad solvents and the effective excluded volume parameter vanishes and may even become negative.

In the many chain problem of strong solutions, the effective potential acting on a test chain is calculated using the same formalism based on the Edwards Hamiltonian. This potential is related to the bare effective potential in the infinite dilute limit via a series expansion which is reminiscent of the Ornstein-Zernike model. This series expansion is represented graphically via a diagrammatic method where the successive diagrams represent interactions involving increasing numbers of intermediate chains. If the solvent mixture is critical, interesting results are obtained for the structure factor of the polymer and a test chain. If the solvent mixture is near criticality, all excluded volume interactions are screened out and chains in the medium feel theta solvent conditions.

This investigation is based upon the Edwards Hamiltonian formalism and gives a qualitative picture of the thermodynamic behavior and structural properties of polymers in mixed solvents. Near critical regions where the fluctuations are strong, one has to rely on an appropriate model to achieve a more rigorous quantitative evaluation of the effects of critical fluctuations on the thermodynamic and the scattering properties of polymers in mixed solvents. This could be done within the framework of field theoretical or renormalization group theory calculations.

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## Figure Captions

**Figure 1:**

Variation of  $\chi'_c$  the critical interaction parameter between solvents  $A$  and  $B$  with the polymer volume fraction  $\phi_1$  for two values of  $\chi_{BP}$  and  $\chi_{AB} = 1$ ,  $N = 100$ ,  $\phi_B = 0.495$   $\epsilon = \chi_{AP} - \chi_{BP} = 0.2$  (see equation (29)).

**Figure 2:**

Variation of  $V_0$  the effective excluded volume parameter with the parameter  $\Delta\chi_0$  for two values of  $\epsilon$  and  $\chi_{BP} = 0.5$ , (see equation (31), the other values are chosen to be the same as above)

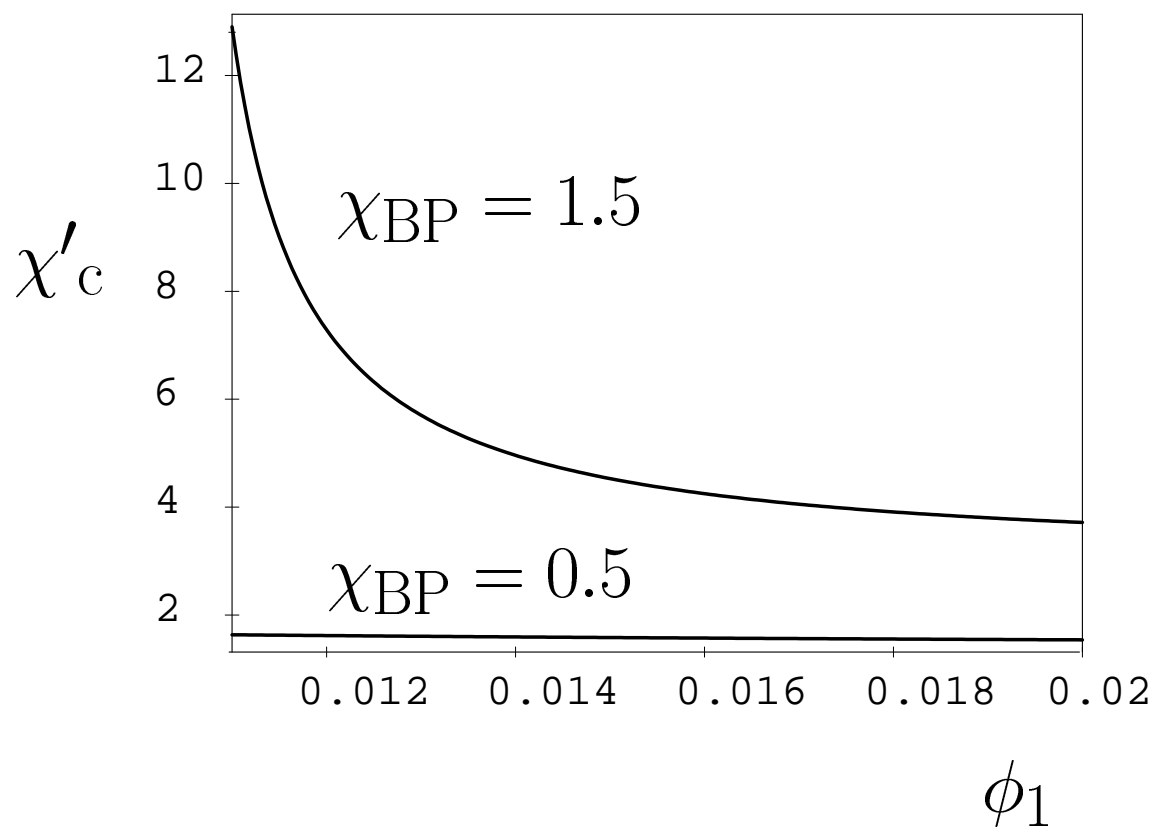
**Figure 3:**

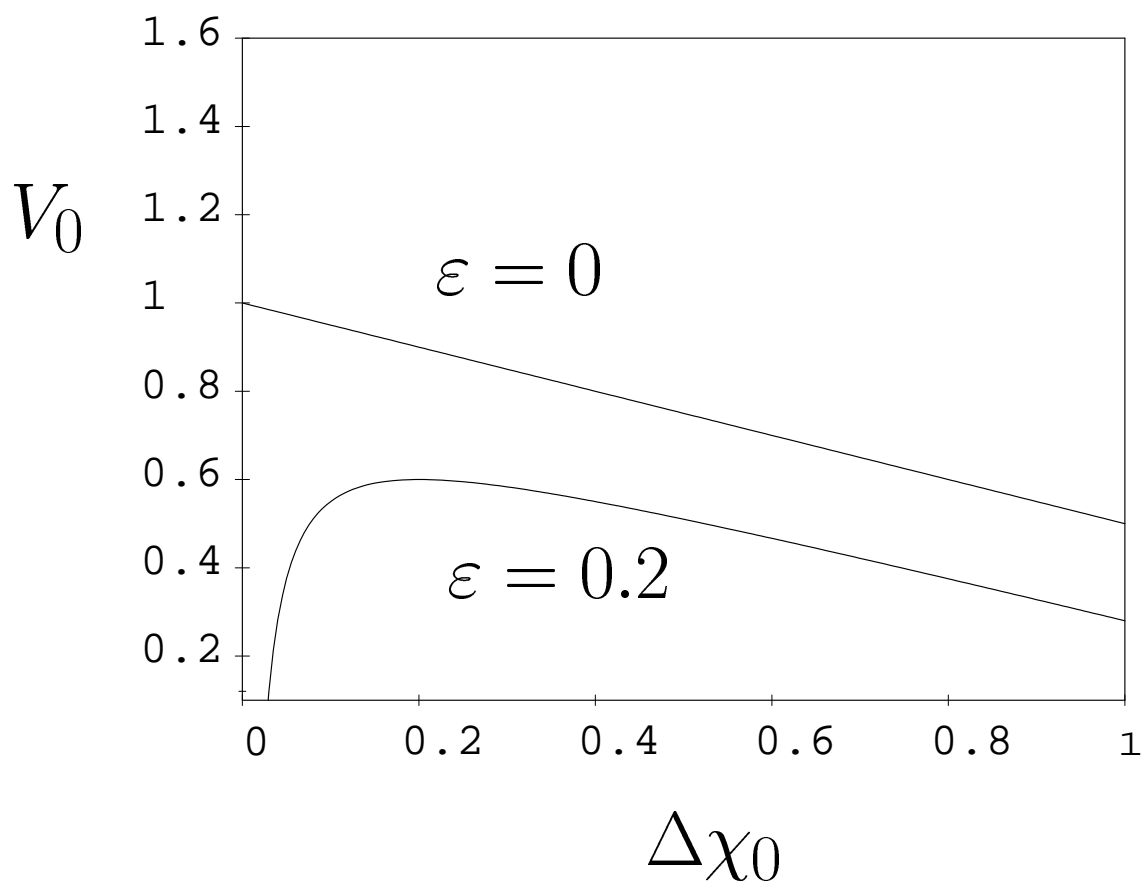
Variation of  $\chi_0$  the effective interaction parameter with the parameter  $\Delta\chi_0$  for two values of  $\epsilon$  and  $\chi_{BP} = 0.5$ , (see equation 33)

**Figure 4:** Variation of  $\xi_0/R_g$  the normalized correlation length for solvent fluctuations with the parameter  $\Delta\chi_0$  for two values of  $\epsilon$  and  $\chi_{BP} = 0.5$ , (see equation (36)) In plotting these figures, we have used  $N = 100$ ,  $\phi_A = \phi_B$  and  $\chi_{AB} = 1$ .

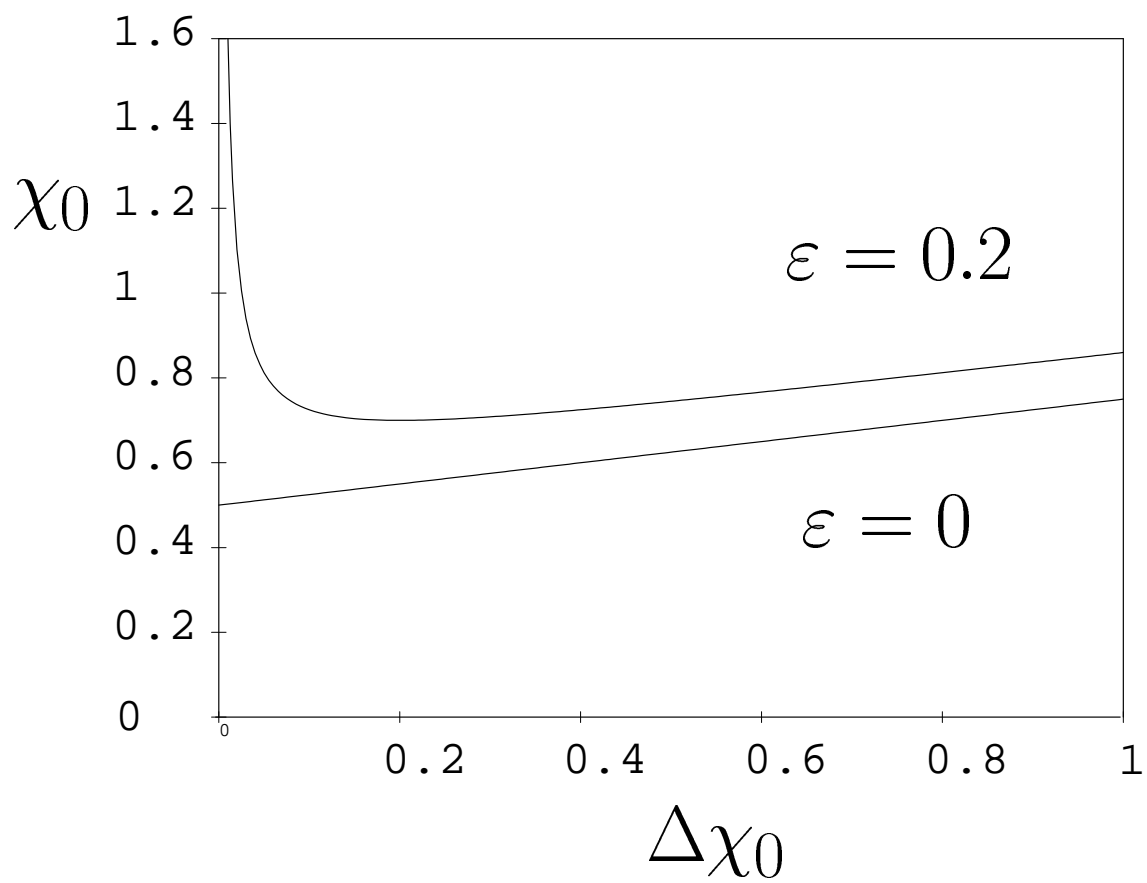
**Figure 5:** Diagrammatic representation of the relationship between the effective potentials in the many chain ( $V$ ) and in the single chain problems ( $V_0$ ) a) Representation of the infinite series of equation (47) b) Representation of equation (48). Vertical thick lines represent the main interacting chain. Vertical dashed lines represent intermediate chains of interaction. Horizontal dashed wavy line is an interaction  $V_0$  Horizontal thick wavy line is an interaction  $V$ .

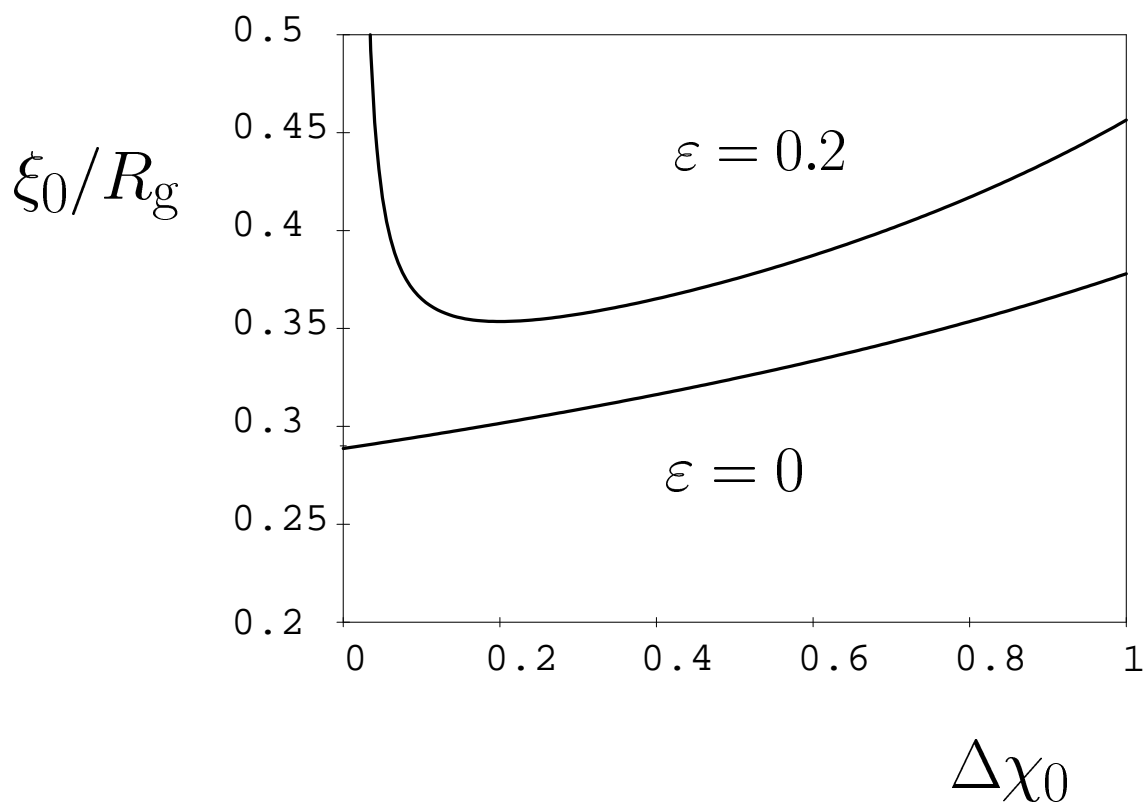
**Figure 6:** Variation of the ratio  $V/V_0$  as a function of  $q\xi$  according to equation (52) where  $\xi$  is the Edwards screening length.











$$\begin{array}{c}
\left| \begin{array}{c} \text{wavy line} \\ V \end{array} \right| = \left| \begin{array}{c} \text{wavy line} \\ V_0 \end{array} \right| + \left| \begin{array}{c} \text{wavy line} \quad \text{wavy line} \\ V_0 \quad V_0 \end{array} \right| + \left| \begin{array}{c} \text{wavy line} \quad \text{wavy line} \quad \text{wavy line} \\ V_0 \quad V_0 \quad V_0 \end{array} \right| + \dots
\end{array}$$

$S_P$                        $S_P$        $S_P$

(Vertical dashed lines connect  $S_P$  to the wavy lines in the diagrams)

$$\begin{array}{c}
\left| \begin{array}{c} \text{wavy line} \\ V \end{array} \right| = \left| \begin{array}{c} \text{wavy line} \\ V_0 \end{array} \right| + \left| \begin{array}{c} \text{wavy line} \quad \text{wavy line} \\ V_0 \quad V \end{array} \right|
\end{array}$$

$S_P$

(Vertical dashed line connects  $S_P$  to the wavy line in the second diagram)

Fig. 1.    b

